

CLAIMS

1. A catalyst composition for polymerization of olefins and copolymerization of olefins with alpha-olefins comprising (a) catalyst precursor comprising at least one Ziegler-Natta compound, at least one metallocene compound, at least one titanate compound and/or at least one alcohol compound, a magnesium compound and a polymeric material, and (b) a cocatalyst comprising an alkylaluminum compound, aluminoxane compound or mixtures thereof.
2. The catalyst composition according to claim 1 wherein the alpha-olefin is selected from the group of alpha-olefins having 1 to 18 carbon atoms including propene, 1-butene, 1-hexene, 1-octene and 4-methyl 1-pentene and mixtures thereof.
3. The catalyst composition according to claim 1 or 2 wherein the Ziegler-Natta compound is represented by the general formula TmX_4 , $TmOX_3$, or TmX_3 , wherein Tm represents titanium, vanadium or zirconium and X represents a halogen atom.
4. The catalyst composition according to claim 3 wherein the Ziegler-Natta compound is titanium tetrachloride, titanium trichloride, vanadium tetrachloride, vanadium trichloride, vanadium oxytrichloride, zirconium tetrachloride and the like.
5. The catalyst composition according to any of the preceding claims wherein the metallocene compound is represented by the general formula $(Cp)_zTmX_y$ wherein Tm represents a transition metal such as titanium, vanadium or zirconium, Cp represents a unsubstituted or substituted cyclopentadienyl ring, X represents a halogen atom, z is 1 or 2, and y is 2 or 3.
6. The catalyst composition according to claim 5 wherein the cyclopentadienyl ring may be unsubstituted or substituted with a hydrocarbyl radical such as alkyl, alkenyl, aryl containing 1 to 20 carbon atoms; such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, amyl, isoamyl, phenyl and the like.

7. The catalyst composition according to claim 5 or 6 wherein the metallocene compound is bis(cyclopentadienyl)titanium dichloride, bis(methylcyclopentadienyl)titanium dichloride, bis(butylcyclopentadienyl)titanium dichloride, bis(pentamethylcyclopentadienyl)titanium dichloride, cyclopentadienyltitanium trichloride, methylcyclopentadienyltitanium trichloride, butylcyclopentadienyltitanium trichloride, pentamethylcyclopentadienyltitanium trichloride, bis(cyclopentadienyl)vanadium dichloride, bis(methylcyclopentadienyl)vanadium dichloride, bis(butylcyclopentadienyl)vanadium dichloride, bis(pentamethylcyclopentadienyl)vanadium dichloride, cyclopentadienylvanadium trichloride, methylcyclopentadienylvanadium trichloride, butylcyclopentadienylvanadium trichloride, pentamethylcyclopentadienylvanadium trichloride, bis(cyclopentadienyl)zirconium dichloride, bis(methylcyclopentadienyl)zirconium dichloride, bis(butylcyclopentadienyl)zirconium dichloride, bis(pentamethylcyclopentadienyl)zirconium dichloride, cyclopentadienylzirconium trichloride, methylcyclopentadienylzirconium trichloride, butylcyclopentadienylzirconium trichloride, pentamethylcyclopentadienylzirconium trichloride and the like.
8. The catalyst composition according to claim 7 wherein the metallocene compound is bis(cyclopentadienyl)titanium dichloride, bis(methylcyclopentadienyl)titanium dichloride, bis(butylcyclopentadienyl)titanium dichloride, bis(pentamethylcyclopentadienyl)titanium dichloride, cyclopentadienyltitanium trichloride, methylcyclopentadienyltitanium trichloride, butylcyclopentadienyltitanium trichloride, or pentamethylcyclopentadienyltitanium trichloride.
9. The catalyst composition according to any of the preceding claims wherein the titanate compound is represented by the general formula $\text{Ti}(\text{OR}^1)_n\text{X}_{4-n}$, wherein R^1 represents an alkyl group, aryl group or cycloalkyl group having 1 to 20 carbon atoms, X represents a halogen atom, n represents a number satisfying $0 < n \leq 4$ and R^1 includes alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and the like.
10. The catalyst composition according to claim 9 wherein the titanate compound is methoxytitanium trichloride, dimethoxytitanium dichloride, tetramethoxytitanium, ethoxytitanium trichloride, diethoxytitanium dichloride, tetraethoxytitanium, propoxytitanium trichloride, dipropoxytitanium dichloride, tripropoxytitanium chloride, tetrapropoxytitanium, butoxytitanium trichloride, dibutoxytitanium dichloride, tetrabutoxytitanium and the like.

11. The catalyst composition according to claim 10 wherein the titanate compound is tetraethoxytitanium, tetrapropoxytitanium, or tetrabutoxytitanium.
12. The catalyst composition according to any of the preceding claims wherein the alcohol is represented by the general formula R^2OH , wherein R^2 is an alkyl group, aryl group or cycloalkyl group having 1 to 20 carbon atoms.
13. The catalyst composition according to claim 12 wherein the alcohol is methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, cyclohexanol, phenol, methylphenol, ethylphenol and mixtures thereof.
14. The catalyst composition according to any of the preceding claims wherein the magnesium compound is a Grignard compound represented by the general formula R^3MgX wherein R^3 is a hydrocarbon group having 1 to 20 carbon atoms and X is a halogen atom, and/or a dialkyl magnesium compound represented by the general formula R^4R^5Mg wherein R^4 and R^5 are each a hydrocarbon group having 1 to 20 carbon atoms.
15. The catalyst composition according to claim 14 wherein the magnesium compound is diethylmagnesium, di-n-propylmagnesium, di-isopropylmagnesium, di-n-butylmagnesium, di-isobutylmagnesium, butylethylmagnesium, dihexylmagnesium, dioctylmagnesium, butyloctylmagnesium, ethylmagnesium chloride, butylmagnesium chloride, hexylmagnesium chloride or mixtures thereof.
16. The catalyst composition according to any of the preceding claims wherein the polymeric material is in the form of particles having a mean particle diameter of about 5 to 1 000 microns and a pore volume of at least about $0.05 \text{ cm}^3/\text{g}$ and a pore diameter of about 20 to 10 000 angstroms and a surface area of about 0.1 to $100 \text{ m}^2/\text{g}$.
17. The catalyst composition according to claim 16 wherein the pore diameter is from about 500 to 10 000 angstroms and the surface area is from about 0.2 to $15 \text{ m}^2/\text{g}$.
18. The catalyst composition according to any of the preceding claims wherein the polymeric material is selected from the group consisting of polyvinylchloride, polyvinylalcohol

polyethylmethacrylate, polymethylmethacrylate, ethylene-vinylalcohol copolymer, polycarbonate and the like.

19. The catalyst composition according to claim 18 wherein the polymeric material is polyvinylchloride.
20. The catalyst composition according to claim 19 wherein the polyvinylchloride has a molecular weight in the range of about 5 000 to 500 000 g/mole.
21. The catalyst composition according to any of the preceding claims wherein the magnesium compound is present in the range of about 0.05 to 20 mmol per gram polymeric material.
22. The catalyst composition to any of the preceding claims wherein the alkylaluminum compound is represented by the general formula $R_n^6AlX_{3-n}$ wherein R^6 represents a hydrocarbon group having 1 to 10 carbon atoms; X represents a halogen and n represents a number satisfying $0 < n \leq 3$.
23. The catalyst composition according to claim 22 wherein the alkylaluminum compound is trimethylaluminum, triethylaluminum, tri-isobutylaluminum or tri-n-hexylaluminum.
24. The catalyst composition according to any of the preceding claims wherein the aluminoxane compound is represented by the general formula $R^7R^8Al-O-AlR^9R^{10}$ wherein R^7 , R^8 , R^9 and R^{10} are either the same or different linear, branched or cyclic alkyl group having 1 to 12 carbons; such as methyl, ethyl, propyl or isobutyl.
25. The catalyst composition according to claim 24 wherein the aluminoxane is methylaluminoxane or modified methylaluminoxane (MMAO).
26. The catalyst composition according to any of the preceding claims wherein the cocatalyst is used in an amount of about 10 to 10 000 in terms moles of aluminum in the cocatalyst to moles of transition metal in the catalyst precursor.

27. A process for polymerization of olefins and copolymerization of olefins with alpha-olefins using a catalyst composition according to any of the preceding claims 1 to 26.
28. The process according to claim 27 wherein the polymerization is performed in gas phase, slurry phase or solution phase.
29. The process according to claim 27 or 28 wherein the polymer product of polymerization has a weight average molecular weight of about 500 to 1000 000 g/mole.